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| 13. ABSTRACT (Maximum 200 words) Chemielelectron spectroscopy has been used to study the associative and rearrangement ionization reactions of a number of metals with O, O ₂ (X ³ Σ _g ⁻) and O ₂ (a ¹ Δ _g) and other atmospheric species. The spectra obtained have been used to identify the main chemiionization channel and to obtain details of the potential surfaces of the reactants and products. Mass spectra, recorded as a function of extraction potential, have also been used to identify primary ions associated with chemiionization reactions. The chemiionization reactions of oxygen atoms with a number of hydrocarbons have also been studied by chemielelectron spectroscopy. Photoelectron spectroscopy has also been used to study in the gas phase the electronic structure of a number of metals and metal oxides which are of importance in the upper atmosphere. Multiphoton spectroscopic studies have also been performed on a number of reactive intermediates. | | | | | |
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This research project was initiated on 1.3.89. and a postdoctoral fellow was appointed.

The initial aim of this work was to study chemielectron and mass resolved ion spectra of lanthanide plus oxidant reactions under thermal conditions. The main oxidants used are molecular oxygen ($O_2(X^3\Sigma_g^-)$ and $O_2(a^1\Delta_g)$) and atomic oxygen ($O(^3P)$). For each reaction, the experimental mass spectrum, together with thermochemical and kinetic modelling calculations, have been used to identify the major chemiionization channel producing the electrons observed in the chemielectron spectrum, and the chemielectron spectra have been interpreted by invoking the classical turning-point mechanism.

In the case of the $Ce + O_2(X^3\Sigma_g^-)$ reaction, the major chemiionization channel, under thermal conditions, has been established as $Ce + O_2 \rightarrow CeO_2^+ + e^-$. The electron spectrum has been interpreted in terms of this process via a classical turning-point mechanism. CeO_2^+ and CeO^+ are observed as reaction products. CeO_2^+ arises almost completely from the above associative ionization reaction, whereas CeO^+ has been shown to arise from more than one reaction in the $Ce + O_2$ reaction scheme. Similar studies have also been completed for the $Ce + O_2(a^1\Delta_g)$ and $Ce + O(^3P)$ reactions and in the latter case the electrons are shown to arise from the reaction $Ce + O \rightarrow CeO^+ + e^-$.

Related work has been completed on the study of the reactions of other lanthanides (La, Pr, Nd, Sm, Eu and Gd) with these oxidants (1,2,3,8). In the case of europium, no ions or electrons were observed for the $Eu + O_2(X^3\Sigma_g^-)$, $Eu + O_2(a^1\Delta_g)$ and $Eu + O(^3P)$ reactions. For the other four lanthanides, studies of the equivalent metal oxidation reactions showed that when each



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metal is reacted with discharged oxygen, the dominant chemiionization channel is the associative ionization reaction $\text{Ln} + \text{O}(^3\text{P}) \rightarrow \text{LnO}^+ + \text{e}^-$. In each case, this conclusion was supported by comparison of the available standard enthalpies for possible chemiionization reactions with the observed high kinetic energy offset of the observed chemielectron band, as well as by mass analysis of the ions produced. Results of the earlier studies made by electron spectroscopy of the reactions of Ce and La with $\text{O}_2(\text{X}^3\Sigma_g^-)$, $\text{O}_2(\text{a}^1\Delta_g)$ and $\text{O}(^3\text{P})$ were discussed in the light of the results of this work.

The results obtained clearly show broad agreement with the trends exhibited in the calculated reaction enthalpies and this has highlighted the predictive ability of such thermodynamic calculations. This is particularly so for the reactions involving metals and O atoms where more reliable thermodynamic data are available than for metal plus O_2 reactions. The major deficiency in the thermodynamic data that has been used to calculate the reaction enthalpies for associative ionization reactions involving a metal and molecular oxygen, is the unavailability of the first ionization energy for many of the metal dioxides. Although values for the first ionization energy of both CeO_2 and GdO_2 are available, the error limits are high and in the case of cerium, this uncertainty is largely responsible for the calculated reaction enthalpy being at least 1 eV too positive.

However, the experimental results can provide a means to estimate an upper limit of the ionization energy for both the respective lanthanide dioxide and its monoxide. This is possible because the measured kinetic energy of the product chemielectrons emerging from the associative ionization reactions between a metal atom and an oxidant provides a lower limit to the true reaction enthalpy. For example, in the case of the associative ionization reaction $\text{Ce} + \text{O}_2(\text{X}^3\Sigma_g^-)$, the reaction enthalpy can be calculated from currently available thermodynamic data as +0.04 eV. This value was

calculated by using the first ionization energy of CeO_2 of (9.8 ± 0.5) eV (1). The measured maximum in the product electron kinetic energy distribution, however, was (0.90 ± 0.04) eV which means that the true reaction enthalpy must be at least -0.90 eV. An upper limit to the first ionization energy can now be calculated if the enthalpy for the process $\text{CeO}_2 \rightarrow \text{Ce} + \text{O}_2$ is known. Since the enthalpies of atomization for all of the lanthanide dioxides are available, this quantity can easily be calculated. In the case of cerium, the enthalpy of dissociation of CeO_2 can be calculated as (9.76 ± 0.22) eV. If the value for the maximum in the kinetic energy distribution for the reaction $\text{Ce} + \text{O}_2 \rightarrow \text{CeO}_2^+ + e$ of (0.90 ± 0.04) eV is subtracted from (9.76 ± 0.22) eV, then an upper limit of the ionization energy of CeO_2 can be determined as (8.86 ± 0.26) eV. This compares with the previous value of (9.8 ± 0.5) eV. This procedure can be carried out for all of the associative ionization reactions studied.

On completion of a study of the lanthanide oxidation reactions, it was decided to modify the ionization chamber of the electron spectrometer used to allow ions and electrons to be sampled from the same reaction cell under a given set of experimental conditions simply by choosing the sign and magnitude of the extraction voltage on the cell. This experimental arrangement is currently being used to study chemiionization reactions of the Group II metal oxides, MO (where $\text{M} = \text{Ca}, \text{Ba}$ and Sr) with water as well as the reaction of calcium, barium and strontium with the oxidants $\text{O}_2(\text{X}^3\Sigma_g^-)$, $\text{O}_2(\text{a}^1\Delta_g)$ and $\text{O}(\text{}^3\text{P})$ (7). The results have been interpreted in terms of a simple thermodynamic model that is consistent with these reactions proceeding via long lived collision intermediates. The electron energy distributions have been interpreted in terms of a simple potential energy model, and the possibility of the inclusion of an associative ionization reaction into a kinetic model of metal chemistry in the upper atmosphere has been considered. This work

will soon be written up for publication although a brief description of the apparatus has been published (7,9).

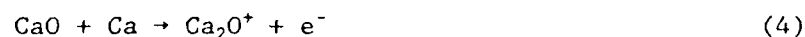
Taking the $\text{Ca} + \text{O}_2(\text{X}^3\Sigma_g^-)$, $\text{Ca} + \text{O}_2(\text{a}^1\Delta_g)$ and $\text{Ca} + \text{O}(\text{}^3\text{P})$ reactions as examples, the electrons and ions seen in the $\text{Ca} + \text{O}_2(\text{X}^3\Sigma_g^-)$ case can be interpreted in terms of the following processes:



Adding $\text{O}_2(\text{a}^1\Delta_g)$ to the $\text{Ca} + \text{O}_2(\text{X}^3\Sigma_g^-)$ reaction mixture reduces the ion and electron yield by removing Ca atoms via the neutral reaction



Chemiiionization can, however, occur via



On adding $\text{O}(\text{}^3\text{P})$ to the system, CaO is produced via



which then undergoes the chemiiionization reaction (4).

The new apparatus proved very useful in distinguishing between primary and secondary ions via the saturation current method and in associating a given primary ion with an observed chemielectron band.

In order to provide a reference against which the results of metal plus oxidant chemielectron spectra can be compared, chemielectron spectra have been recorded for some chemiiionization reactions occurring in low pressure O atom/hydrocarbon gas-phase systems. The chemielectron spectra obtained have been used to elucidate processes which lead to the formation of primary ions in O + hydrocarbon reaction schemes. In addition to the well-established $\text{CH}(\text{X}^2\Pi) + \text{O} \rightarrow \text{HCO}^+ + \text{e}^-$ reaction, evidence has been obtained for the existence of the recently suggested $\text{CH}(\text{}^4\Sigma^-) + \text{O} \rightarrow \text{O} \rightarrow \text{HCO}^+ + \text{e}^-$ route. As well as these reactions, spectral bands have been observed for the reaction $\text{C}_2^* + \text{CH}_3 \rightarrow \text{C}_3\text{H}_3^+$

+ e⁻ in a low pressure flow system. It is shown that the experimental spectra are consistent with two excited states of C₂ reacting by this process. This work is virtually complete and will be written up shortly for publication.

Three other papers have also been accepted for publication on the study of short-lived molecules of atmospheric importance by photoelectron spectroscopy (4-6). For example, vacuum ultraviolet photoelectron spectra have been recorded for the F + NH₂OH reaction at different reaction times. At short reaction times, three bands associated with NH₂O were observed, whereas at longer reaction times one band associated with HNO was seen. The NH₂O bands were assigned with the aid of *ab initio* molecular orbital calculations which used an essentially planar equilibrium geometry for the neutral ground state. The HNO band showed resolved vibrational structure which was analysed in terms of excitation of the N-O stretching and HNO deformation modes in HNO⁺(X²A'). The first adiabatic and vertical ionization energies of HNO(X¹A') were measured as (10.18 ± 0.01) and (10.56 ± 0.01) eV respectively. Assignment of the vibrational structure was confirmed by recording the first photoelectron band of DNO, prepared from the F + ND₂OD reaction.

As a preliminary to the study of NaO and KO in the gas-phase with photoelectron spectroscopy, the dissociation energies and the low-lying ²Σ⁺-²Π electronic state separations were calculated for these molecules with basis sets of approximately TZ quality at the SCF and CISD levels (10). Corrections were made for size-consistency and basis set superposition errors. Particular attention was paid to the effect of internal basis set superposition error (IBSSE) on the calculated properties. Two methods were devised to estimate the part of IBSSE due to symmetry lowering in a counterpoise correction with the presence of a ghost centre. Calculated results showed a large IBSSE associated with KO, at the correlated level, which was due to such symmetry

lowering in the K^+ calculations. For both molecules, the ground state was computed to be a $^2\Pi$ state and reasonably good agreement was obtained between the calculated and available experimental values for the $^2\Sigma^+-^2\Pi$ separations. The computed values of $D_0(\text{NaO}, X^2\Pi)$ and $D_0(\text{KO}, ^2\Pi)$ at the highest levels of theory used are both lower than the available experimental values derived from electron impact mass spectrometry. This is attributed to a small population of the $^2\Sigma^+$ state under the conditions of the mass spectrometric experiments.

Recently a multiphoton ionization (MPI) spectrometer has been constructed with the long term aim of adding a molecular beam source to allow MPI studies to be performed on high temperature molecules, notably diatomic metal oxides, prepared in a supersonic jet. During the development of this apparatus, previously unobserved excited states of three molecules $\text{NS}(11)$, $\text{SO}(12)$, and $\text{S}_2(13)$ have been investigated using laser multiphoton ionization. Taking the SO molecule as an example, Rydberg states of this molecule in the region $62,500\text{--}67,500\text{ cm}^{-1}$ above the neutral ground state have been studied using both $(3+1)$ and $(2+1)$ resonance enhanced multiphoton ionization (MPI) spectroscopy. Band assignment has been assisted by recording spectra with both linearly and circularly polarized radiation, by simulation of rotational band contours and by calculating quantum defects for the observed Rydberg states.

Transitions to four Rydberg states (the $^3\Delta(4p\pi)$, $^3\Pi(3d\delta)$, $^3\Pi(3d\sigma)$ and $^3\Phi(3d\delta)$ states) have been observed corresponding to promotion of an electron from the outermost occupied π molecular orbital in $\text{SO}(X^3\Sigma^-)$ to the $4p\pi$, $3d\delta$, and $3d\sigma$ Rydberg orbitals. For each state, spectroscopic constants have been derived from the experimental spectra. A $(2+2)$ MPI spectrum of a known valence state, the $\text{B}^3\Sigma^-, v'=8$ state, has also been obtained.

Papers arising from this research

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